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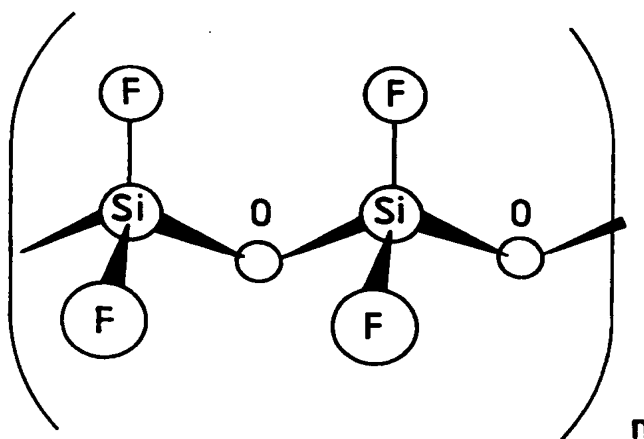
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(54) A dielectric, a manufacturing method thereof, and semiconductor device using the same

(57) A silicon oxide fluoride film having Si-F bonds and Si-O bonds is used for dielectric insulators for the wiring of semiconductor devices. Dielectric films are formed using SiF_2X_2 gas (X = H, Cl, Br, OCH_3 , OC_2H_5 , and OC_3H_5) as a reactant.

Using this dielectric, semiconductor devices having a small wiring delay and high reliability can be manufactured, because the silicon oxide fluoride film having Si-F bonds and Si-O bonds has a smaller dielectric constant than a silicon oxide fluoride film having Si-Si bonds and O-F bonds.

FIG. 1



$$\epsilon = 1.88$$

Description

Background of the Invention

The present invention relates to a dielectric, a manufacturing method thereof, and a semiconductor device, especially to a dielectric with a low dielectric constant suitable for moderating wiring delay of signals and improving durability of semiconductor integrated circuits and the like.

In accordance with the conventional manufacturing process for semiconductor devices, a trial for moderating the wiring delay of signals has been performed, and is as follows. The signals are transmitted through wiring, and an organic film with a low dielectric constant is used to insulate the wiring. However, the insulation of the wiring by the organic film is hardly used because of problems with the durability of the organic film.

Currently, to improve durability, methods for preparing dielectric films composed of silicon, oxygen, and fluorine (called SiOF films hereinafter) have been developed, for instance, the method using silicon tetrafluoride (SiF_4) and oxygen as reacting gases, as disclosed in "Preparation of SiOF Films with Low Dielectric Constant by ECR Plasma Chemical Vapor Deposition" p.158, Extended Abstract of the 1993 Conference on Solid State Devices and Materials (1993). Further, another method of adding gases from the fluorine group to the gases necessary for forming a silicon oxide film is disclosed in "Formation Mechanism of F-added SiO_2 Films using Plasma CVD" p.133, The 16th Proceedings of Symposium on Dry Process (1994).

In connection with the conventional SiOF films, the fluctuation in the dielectric constant of the films, is so large that it is not possible to form films with a low dielectric constant. Further, the humidity resistance of the films is low.

The present invention has been developed with consideration of the above problems.

It is the underlying problem of the present invention to provide new SiOF dielectrics, methods for manufacturing these dielectrics, and their use, particularly for or in semiconductor devices.

The above problem is solved according to the independent claims. The dependent claims relate to preferred embodiments of the concept of the present invention.

Summary of the Invention

The dielectric according to the present invention comprises one or more silicon oxide fluoride compounds, having covalent bonds of fluorine atoms and silicon atoms.

Further, in accordance with a method for manufacturing the dielectric according to the present invention, an SiOF film is formed by supplying an amount of energy to a gas which contains SiF_2X_2 which does not

dissociate the covalent bonds of fluorine atoms and the silicon atoms of the SiF_2X_2 .

Furthermore, in accordance with the semiconductor device according to the present invention, dielectric bodies comprising silicon oxide fluoride compounds, having covalent bonds of fluorine atoms and silicon atoms, are provided between a plurality of wirings which are located on the substrate of the semiconductor device.

The dielectric constant of a substance is the sum of components based on orientation polarization, ionic polarization, and electronic polarization. The main component of the dielectric constant of a non-oriented substance such as an SiO_2 or SiOF film is almost the same as the dielectric constant based on electronic polarization. The dielectric constant based on the electronic polarization can be obtained from the atomic refraction of the constituent atoms, or the electronic group refraction of the bonds between the atoms.

Fig. 1 illustrates the molecular structure of an SiOF film according to the present invention, and Figs. 2-8 illustrate molecular structures of conventionally known films of SiO , SiO_2 , or SiOX ($\text{X} = \text{OF}, \text{H}, \text{OH}, \text{Cl}$). In said Figs. 2-8, the specific dielectric constants ϵ are shown calculated from the respective atomic refractions. The atomic fraction of F is calculated by subtracting the atomic refraction of C from the molecular refraction of CF_4 . The atomic fraction of Si is calculated by subtracting the atomic refraction of F from the molecular refraction of SiF_4 . The specific dielectric constant ϵ of the SiOF film is smaller than that of SiO and SiO_2 films as shown in Figs. 2-8. Furthermore, in accordance with the present invention, the dielectric constant ϵ of the molecular structure of SiOF films having covalent Si-F bonds is smaller than that of the molecular structure of SiOF films having the covalent Si-O bonds.

Fig. 9 shows dissociation energies of various bonds. The O-F bond is weaker than the Si-F bond by approximately 1/3. Therefore, an SiOF film having Si-F bonds has a smaller ϵ and is chemically more stable than an SiOF film having O-F bonds.

In order to form an SiOF film with a molecular structure having Si-F bonds, SiF_2X_2 molecules are used. These molecules have at least two Si-F bonds and another two Si-X bonds, X being an atom or an atomic group. The Si-X bonds have a smaller bond energy than Si-F bond energy. As shown in Fig. 9, bond energies of Si-H, Si-Cl, Si-O bonds are smaller than the bond energy of Si-F bonds. Accordingly, molecules of Si-X wherein X is any of H, Cl, OCH_3 , OC_2H_5 , OC_3H_7 , and the like are preferable.

When using SiF_2X_2 molecules wherein the bond energy of the Si-X bond is smaller than the bond energy of the Si-F bond, conditions can be established under which the Si-F bonds are kept unchanged but the Si-X bonds dissociate.

In practice, the reaction temperature of a thermal CVD apparatus or the input power of a plasma treating apparatus are controlled so as to bring up 541 kJ per

one mole of SiF_2X_2 molecule, wherein the Si-F bonds do not dissociate. In the above case, oxygen is combined with the Si atom which has two Si-F bonds, and the X atoms dissociate. Furthermore, residual uncombined oxygen valences form a bond with a similar Si in another SiF_2X_2 molecule. Accordingly, SiOF films having a molecular structure wherein F is combined with Si as shown in Fig. 1 can be formed.

As shown in Fig. 9, the bond energy of the Si-H bond is smaller than the bond energies of Si-Cl, and Si-O bonds. Therefore, using a molecule of Si-X wherein the X is H, the margins of the operating conditions can be extended.

Brief Description of the Drawings

Fig. 1 illustrates schematically the molecular structure of an SiOF film of the present invention,
 Fig. 2 illustrates schematically the molecular structure of a conventional SiO(OF) film,
 Fig. 3 illustrates schematically the molecular structure of a conventional SiO_2 film,
 Fig. 4 illustrates schematically the molecular structure of a conventional SiOCl film,
 Fig. 5 illustrates schematically the molecular structure of a conventional SiO film,
 Fig. 6 illustrates schematically the molecular structure of a conventional SiOH film,
 Fig. 7 illustrates schematically the molecular structure of a conventional SiOF film,
 Fig. 8 illustrates schematically the molecular structure of a conventional SiO(OH) film,
 Fig. 9 indicates dissociation energies of various bonds,
 Fig. 10 is a schematic cross-section of an ECR-CVD apparatus used in the present invention for forming SiOF films,
 Fig. 11 is an infrared absorption spectrum of the SiOF film of the present invention,
 Fig. 12 is a schematic cross-section of a parallel plate type RF-CVD apparatus used in the present invention for forming SiOF films,
 Fig. 13 is a schematic cross-section of an ICP-CVD apparatus used in the present invention for forming SiOF films,
 Fig. 14 schematically illustrates a condition according to the present invention, wherein wires on a semiconductor substrate are covered with the SiOF film,
 Fig. 15 schematically illustrates a condition according to the present invention, wherein wires on a semiconductor substrate are covered with the SiOF films, which are formed by overlapped sputtering,
 Fig. 16 schematically illustrates a condition according to the present invention, wherein wires on a semiconductor substrate are covered with a planarized SiOF film,
 Fig. 17 is a graph indicating the relationship between the dielectric constant and HWHH (Half

Width at Half Height) of the SiOF film of the present invention,

Fig. 18 is a graph indicating the relationship between the specific dielectric constant and the density of the SiOF film of the present invention,

Fig. 19 is a graph indicating the relationship between the density and the dielectric breakdown electric field of the SiOF film of the present invention,

Fig. 20 is a graph indicating the relationship between the specific dielectric constant and the desorption amount according to the present invention,

Fig. 21 is a schematic cross-section of an SRAM according to the present invention, wherein the SiOF film is used,

Fig. 22 is a schematic cross-section of a DRAM according to the present invention, wherein the SiOF film is used, and

Fig. 23 is a plan view of a memory cell of the DRAM shown in Fig. 22.

Description of the Preferred Embodiments

The present invention is explained in detail referring to the figures hereinafter.

Embodiment 1

Fig. 10 is a schematic cross-section of an Electron Cyclotron Resonance (ECR)-CVD apparatus, which is one of CVD apparatus used for forming SiOF films. The apparatus comprises a plasma generating chamber 2 having a microwave introducing window 1, a reaction chamber 3, a magnetic field generating coil 4, reaction gas inlets 5 and 6, a holder 8 holding a substrate 7, and a high frequency power source for supplying high frequency waves to the substrate 7.

First, a process for forming an SiOF film using silicon tetrafluoride (SiF_4) and oxygen (O_2) gas is explained. From the reaction gas inlets 5 and 6, O_2 by 200 ml/min and SiF_4 by 40 ml/min are introduced respectively into the reaction chamber 3. The pressure in the reaction chamber 3 is adjusted at 0.2 Pa by controlling the amount of exhaust gas. The exhaust gas system is not shown in Fig. 10. A magnetic field of 0.0875 T is generated in the plasma generating chamber 2 by the magnetic field generating coil 4, and ECR plasma is generated by introducing microwaves of 2.45 GHz so that said SiOF film is formed on the surface of the substrate because of reaction between O_2 and SiF_4 . In this case, a p-type Si substrate of 126 mm in diameter is used as the substrate. The introduced microwave power (P_μ) is 600 W.

The film depositing rate (D.R.) increases proportional to the introduced microwave power (P); for instance, D.R. is 0.2 $\mu\text{m}/\text{min}$ at 600 W of P_μ . The specific dielectric constant ϵ of the formed film is approximately 3.5. The bonding conditions of the formed film

are such that the Si-Si bonds are 10 % of the O-Si-O bonds, and the Si-O-F bonds are 30 % of the Si-F bonds. The specific dielectric constant ϵ can be measured by the formation of an aluminum electrode on the formed film. The bonding conditions of the formed film can be measured by means of fluorescent X ray (XPS) analysis or nuclear magnetic resonance (NMR) analysis.

Next, a method for forming an SiOF film by introducing silane difluoride (SiH_2F_2), according to an embodiment of the present invention, is explained. Conditions for forming SiOF film are the same as those above process which uses SiF_4 . The film deposition rate does not depend on the introduced microwave power, but increases proportional to the amount of introduced SiH_2F_2 gas. When the SiH_2F_2 gas is introduced at a rate of 40 ml/min, the film deposition rate D.R. is equal to 0.38 $\mu\text{m}/\text{min}$, approximately twice of the rate when SiF_4 is used. The reason why the film deposition rate increases when using SiH_2F_2 gas is because the dissociation energy of SiH_2F_2 is lower than that of SiF_4 .

Fig. 11 indicates infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4 , respectively. In the case of SiF_4 (hereinafter case: B), the center of the Si-O vibration is at 1065 cm^{-1} , and with said half width at half height (HWHH) at a lower wave number side is 33 cm^{-1} , although slight moisture (O-H) can be observed.

On the other hand, in the case of SiH_2F_2 (case: A), the center of the Si-O vibration is at 1080 cm^{-1} , and with said half width at half height (HWHH) at a lower wave number side is 24 cm^{-1} . A larger wave number indicates a stronger bond of Si-O, and a smaller WHWW indicates a simpler network with fewer kinds of bonds.

When the bonding condition is measured by fluorescent X ray (XPS) analysis and nuclear magnetic resonance (NMR) analysis, no Si-Si bonds and Si-O-F bonds can be observed. Accordingly, the structure of the film is mostly composed of Si-O bonds and Si-F bonds as shown in Fig. 1. The reason why O-H bonds are not observed in the infrared spectrum is because the structure does not contain weak Si-O-F bonds.

The ϵ of the formed film is approximately 3.2. The ϵ is a value obtained by multiplying an estimated ϵ (= 1.88) of SiOF film shown in Fig. 1 by a conversion ratio η (= 1.76) of ϵ of SiO_2 film (= 2.27), estimated from atomic refraction and ϵ of observed glassy SiO_2 (= 4.0).

As explained above, when the SiOF film is formed by introducing silane difluoride (SiH_2F_2), the deposition rate of the film increases, and the dielectric film having preferable chemical stability such as moisture-resistance and a low dielectric constant can be formed because the formed SiOF film is mostly composed of Si-O bonds and Si-F bonds.

Embodiment 2

When a film is formed under the same conditions as in the above embodiment 1 except introducing silicon

dichloride difluoride (SiF_2Cl_2) instead of SiH_2F_2 , an SiOF film can be formed, wherein no Cl is observed. The deposition rate of the film is almost the same as the rate when SiH_2F_2 is used, and D.R. = 0.36 $\mu\text{m}/\text{min}$. The ϵ is approximately 3.3, which is slightly higher than that in the case of using SiH_2F_2 . That means, when SiF_2Cl_2 is used, an insulator film having a lower dielectric constant than that of the insulator film obtained by using SiH_2F_2 can be formed.

Furthermore, when a film is formed under the same conditions as in the embodiment 1 except introducing silicon dibromide difluoride (SiF_2Br_2) instead of SiH_2F_2 , an SiOF film, wherein no Br is observed, can be formed. The deposition rate of the film is almost the same as the rate in the case of using SiH_2Cl_2 , and D.R. = 0.36 $\mu\text{m}/\text{min}$. Therefore, a dielectric film having a low dielectric constant ϵ such as approximately 3.3 can be formed.

Embodiment 3

When a film is formed under the same conditions as in the embodiment 1 except introducing dimethoxy silicon difluoride ($\text{SiF}_2(\text{OCH}_3)_2$) instead of SiH_2F_2 , an SiOF film, wherein no C is observed, can be formed. The deposition rate of the film is approximately the same as the rate in the case of using SiH_2F_2 , and D.R. = 0.36 $\mu\text{m}/\text{min}$. The ϵ is slightly higher than in the case of using SiH_2F_2 and is approximately 3.3.

When a film is formed under the same conditions as in the embodiment 1 except introducing diethoxy silicon difluoride ($\text{SiF}_2(\text{OC}_2\text{H}_5)_2$) instead of SiH_2F_2 , an SiOF film, wherein C is hardly observed, can be formed. The deposition rate of the film D.R. is 0.36 $\mu\text{m}/\text{min}$, and is slower than that in the case of using SiH_2F_2 . The reason of the slower D.R. is because $\text{SiF}_2(\text{OC}_2\text{H}_5)_2$ has a lower vapor pressure at room temperature than SiH_2F_2 . Therefore, if the temperature of the source vessel and the piping is elevated so as to make it possible to introduce the necessary amount of $\text{SiF}_2(\text{OC}_2\text{H}_5)_2$, 40 ml/min, the D.R. increases to 0.36 $\mu\text{m}/\text{min}$. The ϵ is approximately 3.3.

When a film is formed under the same conditions as in the embodiment 1 except introducing dipropoxy silicon difluoride ($\text{SiF}_2(\text{OC}_3\text{H}_7)_2$) instead of SiH_2F_2 , an SiOF film can also be formed. However, the temperature of the source vessel and the piping must be elevated so as to make it possible to introduce the necessary amount of $\text{SiF}_2(\text{OC}_3\text{H}_7)_2$, 40 ml/min. In this case, the D.R. is 0.36 $\mu\text{m}/\text{min}$, and the ϵ is approximately 3.3.

In accordance with the study by the present inventors, the conditions of coating a substrate surface when the SiOF film is formed on the substrate having an uneven surface become more preferable depending on using source materials in the order of $\text{SiF}_2(\text{OC}_3\text{H}_7)_2$, $\text{SiF}_2(\text{OC}_2\text{H}_5)_2$, ($\text{SiF}_2(\text{OCH}_3)_2$), and SiH_2F_2 .

Embodiment 4

Fig. 12 illustrates schematically the cross-section of a parallel plate type RF (RF: radio frequency)-CVD apparatus for forming an SiOF film. The apparatus comprises a reaction chamber 11, reaction gas inlets 5 and 6, a holder 12 for holding and heating a substrate 7, and a frequency power source 13 for supplying high frequency waves for plasma generation.

First, a process for forming an SiOF film from SiH_2F_2 and nitrogen monoxide (N_2O) gas using the present apparatus is explained hereinafter.

The film is formed by introducing N_2O gas at a rate of 800 ml/min and SiH_2F_2 at a rate of 200 ml/min through the reaction gas inlets 5 and 6, respectively. The pressure in the reaction chamber 3 is adjusted at 200 Pa by controlling the amount of the exhaust gas (the exhaust gas system is not shown in the figure). The SiOF film is formed on a substrate by generating plasma by supplying high frequency waves of 13.6 MHz at 400 W to the upper electrode 14, and reacting N_2O with SiH_2F_2 . The temperature of the substrate is kept at 350 °C.

When SiF_4 is used, the film is scarcely formed. However, when SiH_2F_2 is used, the film can be formed with a deposition rate D.R. of 0.20 $\mu\text{m}/\text{min}$. When O_2 is used instead of N_2O with SiH_2F_2 , the SiOF film can be formed, but the deposition rate D.R. is less than 0.1 $\mu\text{m}/\text{min}$. The film is scarcely formed when SiF_4 is used, because the bond energy of Si-F is large. However, the SiOF film can be formed by RF plasma using SiH_2F_2 , because SiH_2F_2 has Si-H bonds of weak bond energy.

As explained above, the deposition rate is increased by using N_2O instead of O_2 , because N_2O has a lower generation energy of active oxygen than O_2 . The dielectric constant ϵ of the formed SiOF film is approximately 3.2.

As described above, the SiOF film having a low dielectric constant can be formed by RF plasma when SiH_2F_2 is used.

Embodiment 5

Fig. 13 illustrates schematically a cross-section of an ICP (ICP: Inductively Coupled Plasma)-CVD apparatus for forming an SiOF film. The apparatus comprises a reaction chamber 15 made of quartz, reaction gas inlets 5, 6, a holder 16 for holding a substrate 7, and a coil 17 for supplying high frequency waves for plasma generation.

First, in order to compare with the present invention, a process for forming SiOF film using SiF_4 and oxygen gas is explained hereinafter. From the reaction gas inlets 5 and 6, O_2 at a rate of 200 ml/min and SiF_4 at a rate of 40 ml/min are respectively introduced into the reaction chamber 15. The pressure in the reaction chamber 15 is adjusted at 0.2 Pa by controlling the amount of exhaust gas (the exhaust gas system is not shown in the figure). Plasma is generated by supplying

high frequency waves of 13.6 MHz at 1 kW to the coil 17 so that the SiOF film is formed on the surface of the substrate by reaction of O_2 and SiF_4 . The film deposition rate D.R. is 0.2 $\mu\text{m}/\text{min}$, and the specific dielectric constant ϵ of the formed film is approximately 3.5. The bonding conditions of the formed film are such that the Si-Si bonds are 10 % of O-Si-O bonds, and Si-O-F bonds are 30 % of the Si-F bonds.

Next, a method for forming an SiOF film by introducing silane difluoride (SiH_2F_2), an embodiment of the present invention, is explained hereinafter. The other conditions for forming the film except the introduced gas are same as in the above-explained process which uses SiF_4 . The film deposition rate D.R. is 0.38 $\mu\text{m}/\text{min}$, and is approximately twice of the case of using SiF_4 . The increase of the film deposition rate is by the reason that the dissociation energy of the SiH_2F_2 is lower than that of the SiF_4 .

Regarding to the infrared absorption spectra of SiOF films formed by SiH_2F_2 and SiF_4 , in a case of SiF_4 as same as the ECR plasma, the center of Si-O vibration is 1065 cm^{-1} , and the half width at half height (HWHH) at a lower wave number side is 33 cm^{-1} . Although slightly, moisture (O-H) can be observed. On the other hand, in a case of SiH_2F_2 (case: A), the center of Si-O vibration is 1080 cm^{-1} , and the half width at half height (HWHH) at a lower wave number side is 24 cm^{-1} .

Furthermore, any Si-Si bond and Si-O-F bond can not be observed in the film formed by SiH_2F_2 . Accordingly, the structure of the film is mostly composed of Si-O bond and Si-F bond. The reason why O-H bond is not observed in the infrared spectrum is because the structure does not contain weak bond of Si-O-F. Further, the ϵ is approximately 3.2 as same as the embodiment 4, and the film having a low dielectric constant can be formed. Furthermore, the film formed in the present embodiment has preferable chemical stability.

As explained above, the SiOF film having a low dielectric constant can be formed by ICP plasma if silane difluoride (SiH_2F_2) is used.

Embodiment 6

In the above described respective embodiments, when wiring 18 provided on the surface of the semiconductor substrate of the semiconductor device is coated with the SiOF film 19 as shown in Fig. 14, the width of concave portion on the surface of the formed film becomes narrower than the width of the interval between the wiring. Therefore, when a second wiring is formed on the film for multilayers wiring, breaking fraction of wire of the second wiring increases and accordingly, production yield of the semiconductor device decreases. In order to prevent the above decrease of the production yield, the sputtering must be overlapped in forming the SiOF film using SiH_4 and O_2 .

As a reference example for forming the film by overlapping the sputtering, a case of forming SiO_2 film with SiH_4 instead of SiF_4 by the apparatus shown in Fig. 10

is explained hereinafter. However, in the above case, high frequency waves of 400 kHz and 400 W are supplied to the substrate from a high frequency power source 9, and other conditions are made as same as the embodiment 1.

The film deposition rate (D.R.) is 0.38 $\mu\text{m}/\text{min}$ when the sputtering is not overlapped, and the film deposition rate when the sputterings are overlapped is 0.27 $\mu\text{m}/\text{min}$, corresponding to a 30 % reduction. The reduced amount of the film deposition is the sputtering rate (S.R.), and, in the above case, the S.R. is 0.11 $\mu\text{m}/\text{min}$. The film forming condition in the above case is shown in Fig. 15. The film forming condition is determined by the ratio of D.R. and S.R. The D.R. can be increased by increasing the amount of introduced SiH_4 , but the S.R. can not be increased even if the amount of O_2 is increased. The specific dielectric constant ϵ of the formed film is approximately 4.0.

On the other hand, when SiOF film is formed with SiH_2F_2 and O_2 , an embodiment of the present invention, the film deposition rate (D.R.) when the sputterings are not overlapped, is 0.38 $\mu\text{m}/\text{min}$, and the D.R. when the sputterings are overlapped is 0.19 $\mu\text{m}/\text{min}$, 50 % reduction. The reduced amount of 0.19 $\mu\text{m}/\text{min}$ is S.R., and is larger than the S.R. in the case when SiH_4 is used. The remarkable increase in the sputtering rate (S.R.) when the sputterings are overlapped is caused by etching of the film by F of SiH_2F_2 . Therefore, D.R. can be increased by increasing the introducing amount of SiH_2F_2 as much as the increasing amount of the S.R. In accordance with the method explained above, wherein the amount of introducing SiH_2F_2 is controlled so as to obtain D.R. of 0.66 $\mu\text{m}/\text{min}$, a film is formed on the surface of the wiring, i.e. when a film is formed on the surface of the wiring with an effective deposition rate of 0.66 $\mu\text{m}/\text{min}$, the film is formed in a condition as shown in Fig. 15. In the above case, the specific dielectric constant ϵ of the formed film is approximately 3.2.

As explained above, if a film is formed with SiH_2F_2 by overlapping the sputtering, not only a film having a low specific dielectric constant can be formed, but also the effective film deposition rate can be increased without increasing power source of the apparatus and others.

Furthermore, in order to decrease the breaking fraction of wire of the second wiring and improve the production yield, a film structure shown in Fig. 16 may be formed by applying a flattening film, or eliminating extra protrusion of the film by etching back, after forming the film shaped as shown in Fig. 15. Instead of the etching back, mechanical-chemical polishing (CMP) can be used.

Embodiment 7

Fig. 17 is a graph indicating a result of the investigation performed by the present inventor. A relationship between dielectric constant ϵ of SiOF film formed under various forming conditions and the half width at half

height (HWHH) at a lower wave number side of Si-O peak in infrared spectrum. The result reveals that there is a strong correlation between the ϵ and the HWHH. In order to form a SiOF film having a low dielectric constant, a film having the half width at half height (HWHH) at a lower wave number side of Si-O peak in infrared spectrum of less than 30 cm^{-1} must be formed.

Embodiment 8

Breakdown voltage (B.V.) of the SiOF film formed with SiF_4 in embodiment 1 is approximately 5 MV/cm. Generally, the breakdown voltage (B.V.) of conventional SiOF film is 9 MV/cm. The breakdown voltage can be improved by forming a film having an intermediate composition between the above described SiOF film and the conventional SiO_2 film.

As a reference example, there is a film forming method using SiH_4 , 20 ml/min, and SiF_4 , 20 ml/min, instead of SiF_4 , 40 ml/min, in embodiment 1. In this case, the film deposition rate (D.R.) of the film is 0.19 $\mu\text{m}/\text{min}$. If the composition of the formed film is in the range between the SiOF film and the conventional SiO_2 film, the specific dielectric constant ϵ of the film is a value of approximately 3.75. However, ϵ of the SiOF film formed with SiF_4 is approximately 3.9. That means, fluorine doping can hardly be achieved even if SiF_4 is used as doping gas of fluorine, F. Because the bond energy of the Si-F bond in SiF_4 is significantly larger than the bond energy of the Si-H bond in SiH_4 , and the energy introduced into the plasma is hardly used for the dissociation of SiF_4 , but used for the dissociation of SiH_4 .

On the other hand, there is a film forming method wherein SiH_4 , 20 ml/min, and SiH_2F_2 , 20 ml/min, are used instead of SiF_4 , 40 ml/min, in embodiment 1 of the present invention. In this case, film deposition rate (D.R.) of the film is 0.38 $\mu\text{m}/\text{min}$. The specific dielectric constant of the formed film was approximately 3.75. That means, the composition of the formed film is in an intermediate of the SiOF film and the conventional SiO_2 film. Because, bond energy of Si-H bond in SiH_2F_2 is almost similar with the Si-F bond in SiF_4 , and the energy introduced into plasma is used evenly for dissociation of both SiH_2F_2 and SiH_4 . The specific dielectric constant ϵ in a range of 3.2 - 4.0 varies as a primary function of flow rate ratio ($\text{SiH}_2\text{F}_2/\text{SiH}_4$). Therefore, the specific dielectric constant can be controlled readily.

As explained above, SiH_2F_2 is further preferable for doping of fluorine.

Embodiment 9

Fig. 21 illustrates schematically a cross-sectional view of a SRAM using an insulator film manufactured by the present invention. The SRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 by a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer

4, 5, and a second transistor adjacent to the first transistor holding the field oxide film 2 between are formed at predetermined locations. Subsequently, a titanium silicide (TiSi_2) film 24 which composes local wiring is formed on the diffused layer 4, 5. Unnecessary portion of the titanium silicide film 24 is eliminated by photolithography and etching. Then, an insulator film such as silicon oxide film (BSPG) containing phosphorus and boron is formed on whole surface of the substrate. A step difference of the insulator film is made gentle by reflow at 750 °C. Subsequently, an SiO_2 film is formed at 450 °C by a plasma CVD method. A planarized passivation insulator film 9 is composed of a BSPG film on the silicon substrate and an SiO_2 film on the BSPG film. The insulator film 9 formed with chemical mechanical polishing (CMP) process. Further, contact holes are formed on the titanium silicide (TiSi_2) film 24 by photolithography and etching. Bit lines made of tungsten and connecting plugs of wiring layer are formed in the contact holes. Next, a pad for connecting lead wire and a first layer of the wiring layer 11 are formed.

After forming the wiring layer 11, an SiOF film (specific dielectric constant is 3.3) is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2 . The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 16, 17 made of tungsten are formed in the contact holes. Subsequently, after forming a second layer of the wiring layer 14 is formed, an insulator film 15 composed of the SiOF film is formed using SiH_2F_2 . Through holes and the plugs 16, 17 made of tungsten are formed on the insulator film 15.

Consecutively, by the same process as the above, a third layer of the wiring layer 20, a third layer of the planarized insulator film 19, plugs 21, a fourth layer of the wiring layer 22, and a fourth layer of the planarized insulator film 23 are formed, respectively.

In accordance with an investigation by the present inventor, a signal delay time of the above SRAM is 22 ps. On the contrary, the signal delay time of the insulator film composed of the SiO_2 film which is formed with SiH_4 is 28 ps, and the signal delay time of the insulator film composed of the SiOF film which is formed with SiF_4 is 25 ps. In an accelerated test equivalent to 100,000 hours, the signal delay time of conventional SRAM fluctuates significantly in a range of 22-36 ps, but the signal delay time of the SRAM of the present invention scarcely changes. Accordingly, signal delay of the SRAM can be decreased and reliability of the SRAM can be improved by using the SiOF film formed with SiH_2F_2 as the insulator film among wiring. The above advantage becomes more significant when the integration of the SRAM is increased, and the distance between the wires becomes finer.

Fig. 22 illustrates schematically a cross-sectional view of a DRAM using an insulator film manufactured according to the present invention. Fig. 23 is a plan view

of a memory cell of the DRAM. In these figures, BL and WL indicate respectively a bit line and a word line. Furthermore, SN cont., and BL cont. indicate respectively a connecting portion to a storage node and a connecting portion to the bit line. SA indicates the memory cell and its shadow area, and X and Y indicate sizes of the memory cell. In a case of 256 Mbit DRAM, x and y are respectively 0.85 μm and 0.65 μm . The DRAM is manufactured by the following process.

After forming a field oxide film 2 on a p-type silicon substrate 1 by a selective oxide method (LOCOS), a first transistor having a gate 7 and n-type diffused layer 4, 5, and a second transistor adjacent to the first transistor holding the field oxide film 2 between are formed at predetermined locations. Subsequently, an insulator film such as silicon oxide film (BSPG) containing phosphorus and boron is formed on whole surface of the substrate. Then, an SiO_2 film is formed by a plasma CVD method. A planarized passivation insulator film 9 is formed by treating a multilayer body composed of the SiO_2 film and the insulator film with a chemical mechanical polishing (CMP) process. Further, contact holes are formed on the planarized passivation insulator film 9. A connecting plug made of phosphorus doped silicon for being connected to the bit line BL, the storage node SN, and the first layer of the wiring layer is formed in the contact holes. Next, a pad for being connected to the bit line BL and the storage node SN and the wiring layer 11 are formed. Both the pad and the wiring layer have a multilayer structure of $\text{TiN}/\text{Al}/\text{TiN}$, and are formed simultaneously.

After forming the wiring layer 11, an SiOF film is formed on the whole surface of the substrate by a plasma CVD method using SiH_2F_2 . The first layer of the planarized insulator film 12 is formed by treating the SiOF film with a chemical mechanical polishing (CMP) process. The contact holes are formed on the planarized insulator film 12, and plugs 13, 14 made of tungsten are formed in the contact holes.

Subsequently, a capacitor is formed. Size of projected area of the capacitor formed portion is 0.65 μm x 0.65 μm . The capacitor has a cylindrical structure of 0.5 μm high in order to increase charge storage capacity. The capacitor is formed by the following process.

A lower electrode of the storage node SN is formed from tungsten film of 0.5 μm thick, which is formed by a CVD method, by manufacturing with photolithography and dry etching. Next, in order to form side electrode of the storage node SN, a SiO_2 film of 0.3 μm thick is deposited. The SiO_2 film is manufactured to a columnar block of 0.4 μm x 0.4 μm by photolithography and dry etching. A tungsten film of 0.2 μm thick is formed on the columnar block by a CVD method. The tungsten film is manufactured to side walls of the storage node SN by etching back. Unnecessary columnar block is eliminated by wet etching. Subsequently, a tantalum pentaoxide (Ta_2O_5) film is formed by a CVD method, and unnecessary portion of the tantalum pentaoxide film is eliminated by photolithography and dry etching. Next, a

titanium nitride (TiN) film of 0.2 μm thick is formed on whole surface. A plate electrode PL is formed by etching back after a plate electrode PL lead out portion of the titanium nitride film is coated with resist by photolithography. At this time, a capacitor of 0.5 μm x 0.5 μm is formed on the plug 14. Next, after forming a TiN film, an Al film, and a TiN film orderly, a wiring layer of periphery circuit is formed by manufacturing the multilayer body with photolithography and dry etching.

Subsequently, an insulator film is formed in order to protect the capacitor and to insulate the second layer of the wiring layer. The insulator film is composed of an oxide film formed with organic silane. Next, through holes and the plugs 16, 17 made of tungsten are formed. By a method using selective growing of tungsten, it becomes possible to form the plugs 16, 17 having respectively different height as shown in Fig. 22.

Next, the third layer of the wiring layer 18 and the pad 19 are formed. Further, the third layer of the planarized SiOF insulator film 20 is formed by the method previously described. Subsequently, in accordance with the above described steps, the plug 21, the fourth layer of the wiring layer 22, and the fourth planarized insulator layer 23 are formed.

According to an investigation by the present inventor, a fraction defective in 200 hours' pressure cooker test of the above described DRAM relating to the present invention is 3 %. On the contrary, when the insulator film is the SiOF film formed with SiH_4 , the fraction defective is approximately 38 %, and when the insulator film is the SiOF film formed with SiF_4 , the fraction defective is approximately 62 %. Accordingly, the reliability of the DRAM can be increased by using the SiOF film formed with SiH_2F_2 as the insulator film.

Furthermore, the present inventor examined TFT characteristics of a TFT using the SiOF film formed with SiH_2F_2 as a gate insulator film of a TFT-LCD, and of a TFT using the SiO_2 film formed with conventional SiH_4 . In accordance with the result, the mobility μ in the case using SiOF film is approximately 0.6 $\text{cm}^2/\text{V} \cdot \text{s}$, and the mobility μ in the case using SiO_2 film is approximately 0.4 $\text{cm}^2/\text{V} \cdot \text{s}$. The difference in μ as above described is caused by fluorine isolated in plasma when SiH_2F_2 is used, which flattens the surface of the formed film.

The SiOF film is preferable as a passivation film for LSI, power transistor, and TFT, because it is hydrophobic.

Embodiment 10

The present inventors investigated the SiOF film manufactured with the same apparatus and method as in embodiment 1 under various reaction pressure, input power, and gas flow rate. Results of the investigation are explained hereinafter.

Fig. 18 is a graph indicating the relationship between the specific dielectric constant and the density of the formed film. The specific dielectric constant depends on the density, and especially, the specific die-

lectric constant can be expressed approximately by a primary function of the density when the density is in a range of 1.8-2.4 g/cm^3 . That means, the dielectric constant can be decreased by lowering the density.

Fig. 19 is a graph indicating the relationship between breakdown voltage and density of the formed film. The film has a sufficient breakdown voltage as an insulator film between wires in a region where the density is larger than 1.8 g/cm^3 .

As explained above, the SiOF film having a density in the range of 1.8-2.4 g/cm^3 is preferable as an insulator film of low dielectric constant.

Embodiment 11

Results of investigations by the present inventors on the desorption amount of the SiOF film in embodiment 10 are explained hereinafter.

Fig. 20 indicates the relationship between the specific dielectric constant of the formed film and the desorption amount of the film when the film is heated at 600 $^\circ\text{C}$. The value of the desorption amount is normalized with the specific dielectric constant of the film formed with SiH_2F_2 in embodiment 1. As Fig. 20 indicates, when the specific dielectric constant is in a range of 2.8-3.2, the desorption amount is a constant. However, when the specific dielectric constant is less than 2.8 or larger than 3.2, the desorption amount increases. When the specific dielectric constant is less than 2.8, coarse portions of the film material is generated in the formed film because of low density, and moisture in air is taken into the coarse portions. Consequently, the desorption amount increases. When the specific dielectric constant is larger than 3.2, moisture in air or hydroxide group in moisture is readily taken into the film because of existing O-F bond Si-Si bond. Consequently, the desorption amount increases.

As explained above, in order to decrease moisture content of the film, use of the film having the specific dielectric constant in a range of 2.8-3.2 is preferable. By using such a film as described above, reliability of semiconductor devices such as LSI and the like can be improved.

SiNF film can be formed by using nitration gas such as N_2 , or NH_3 instead of oxidation gas. When an SiN film formed with SiH_2F_2 and nitration gas such as N_2 , or NH_3 is used as a TFT gate film, more preferable characteristics can be obtained than a TFT using an SiN film formed with SiH_4 as a gate film. As explained above, SiH_2F_2 is preferable for forming a gate insulator film of semiconductor.

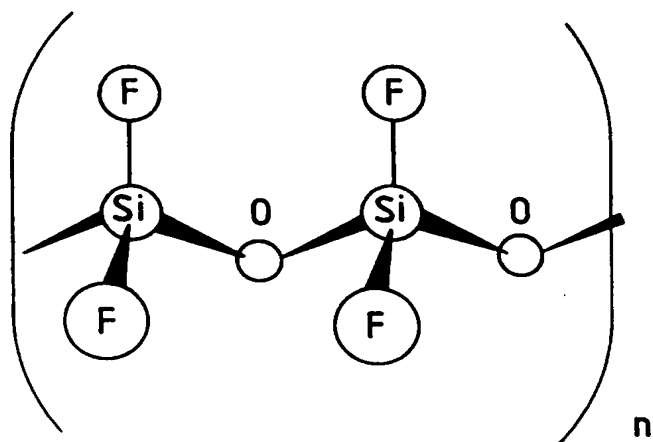
In accordance with the present invention, a dielectric film having a low dielectric constant and high reliability can be formed, and consequently, a semiconductor device of less wiring delay of signal and a semiconductor device having preferable characteristics can be manufactured. Because the dielectric film having a low dielectric constant and high reliability can be formed

effectively, such an advantage as reducing manufacturing cost of the semiconductor devices can be realized.

Claims

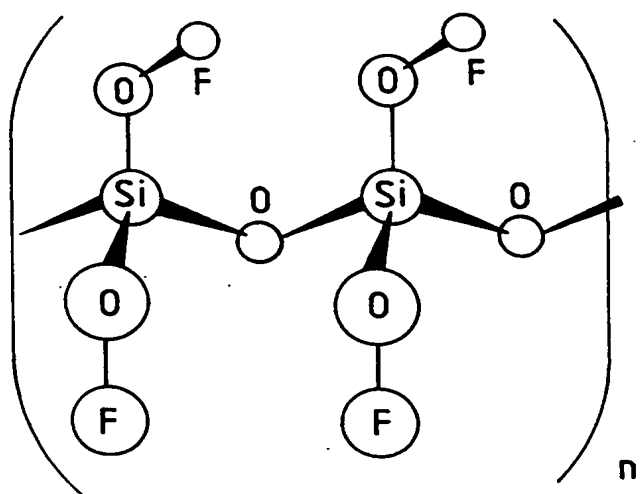
1. A dielectric comprising a silicon oxide fluoride compound having a covalent bond between a fluorine atom and a silicon atom.
2. Dielectric according to claim 1, wherein the silicon oxide fluoride compound has an additional covalent bond between the silicon atom and an oxygen atom.
3. Dielectric according to claim 1 and/or 2, which has a half width at half height of equal to or less than 30 cm^{-1} at a region in the low frequency range of the infrared spectrum.
4. Dielectric according to one or several of claims 1 to 3, which has a density in a range of $1.8\text{-}2.4\text{ g/cm}^3$.
5. Dielectric according to one or several of claims 1 to 4, which has a dielectric constant in the range of $2.8\text{-}3.2$.
6. A method for manufacturing a dielectric particularly those of claims 1 to 5, comprising the following steps: introducing a gas containing SiF_2X_2 gas onto a substrate, and supplying energy to the gas which does not lead to a dissociation of the covalent bonds between the fluorine atoms and the silicon atoms in the SiF_2X_2 .
7. The method according to claim 6, wherein an SiF_2X_2 compound is used wherein X is selected from H, Cl, Br, OCH_3 , OC_2H_5 , and OC_3H_7 .
8. The method according to claim 6 and/or 7, wherein said energy supplied is less than 541 kJ per 1 mol of SiF_2X_2 .
9. The method according to one or several of claims 6 to 8, wherein the energy is supplied by means of a CVD apparatus.
10. The method according to one or several of claims 6 to 8, wherein the energy is supplied by means of a plasma treating apparatus.
11. The method according to one or several of claims 6 to 8, wherein overlapping sputtering processes are applied.
12. The method according to claim 10, wherein the plasma is generated by radio waves.
13. Dielectric according to one or several of claims 1 to 5, obtainable according to the methods of claims 6 to 12.
14. Semiconductor device, comprising a plurality of wirings located on the surface of a semiconductor substrate, and a dielectric located at the intervals between the wirings, characterized in that the dielectric is a dielectric according to one of claims 1 to 5 and 13.
15. Semiconductor device, particularly according to claim 14, comprising a plurality of wirings located on the surface of a semiconductor substrate, and a dielectric comprising a silicon oxide fluoride compound, which has a half width at half height of equal to or less than 30 cm^{-1} in the low frequency region of the infrared spectrum.
16. Use of the dielectric according to claims 1 to 5 for manufacturing LSIs power transistors, TFTs and similar semiconductor elements and circuits.

FIG. 1



$$\epsilon = 1.88$$

FIG. 2



$$\epsilon = 2.00$$

FIG. 3

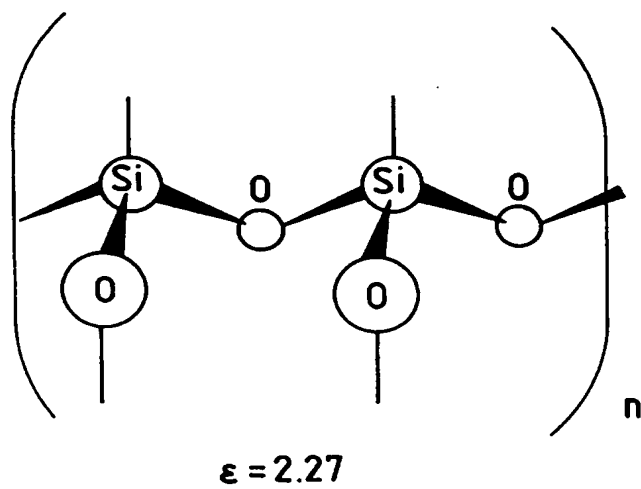


FIG. 4

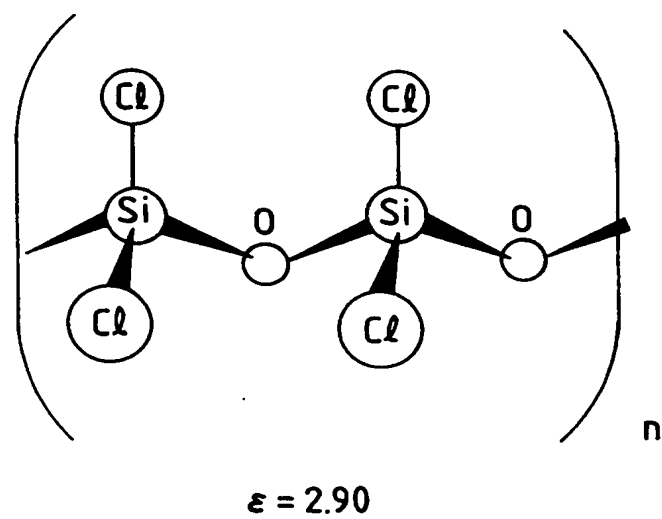
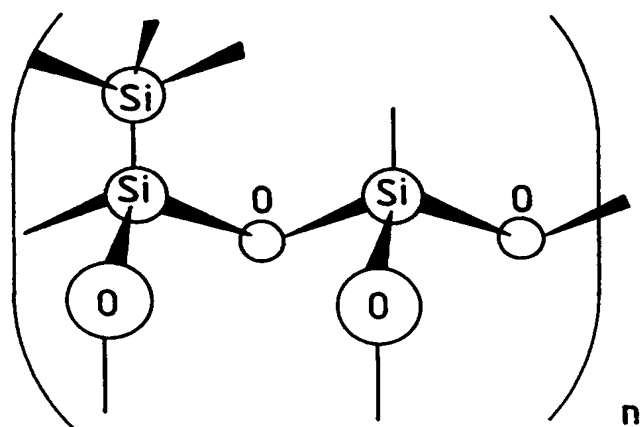
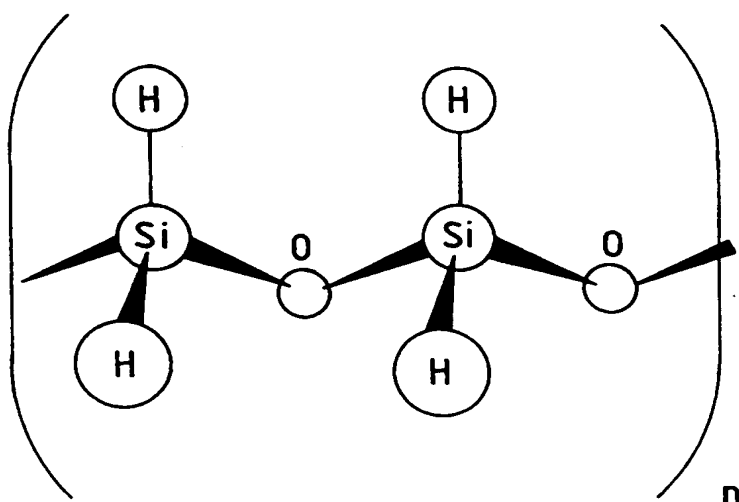


FIG. 5



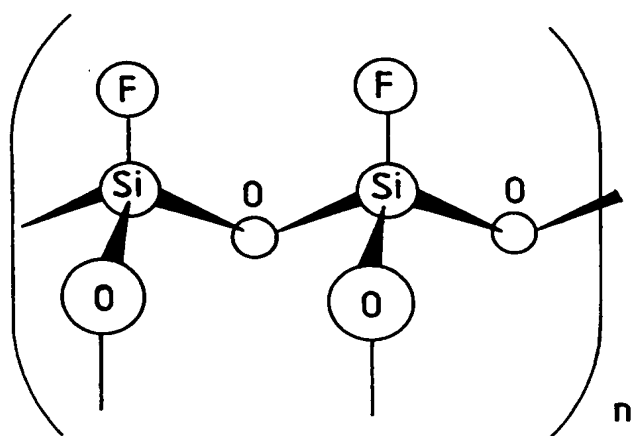
$$\epsilon = 2.35$$

FIG. 6



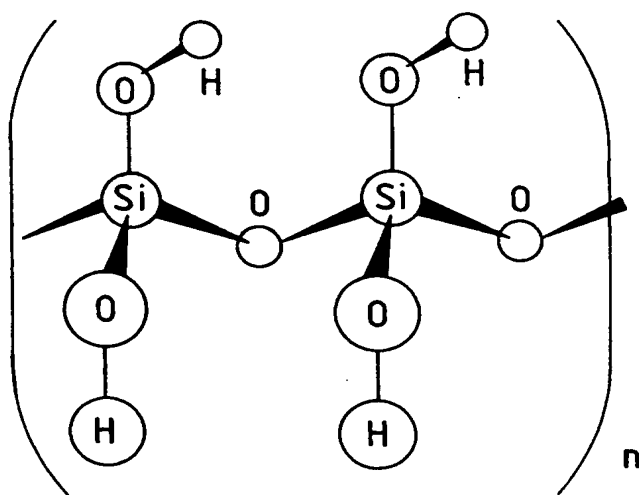
$$\epsilon = 2.19$$

FIG. 7



$$\epsilon = 2.09$$

FIG. 8



$$\epsilon = 2.61$$

FIG. 9

BOND	ENERGY (KJ/mol)	BOND	ENERGY (KJ/mol)
Si - F	541.0	Si - H	294.6
C - H	413.4	O - F	184.9
Si - O	369.0	Si - Si	176.6
Si - Cl	358.6	F - F	153.0
C - O	351.5	O - O	1386
$O_2 \rightarrow O^*$	351.5	$N_2O \rightarrow O^*$	305.4

FIG. 10

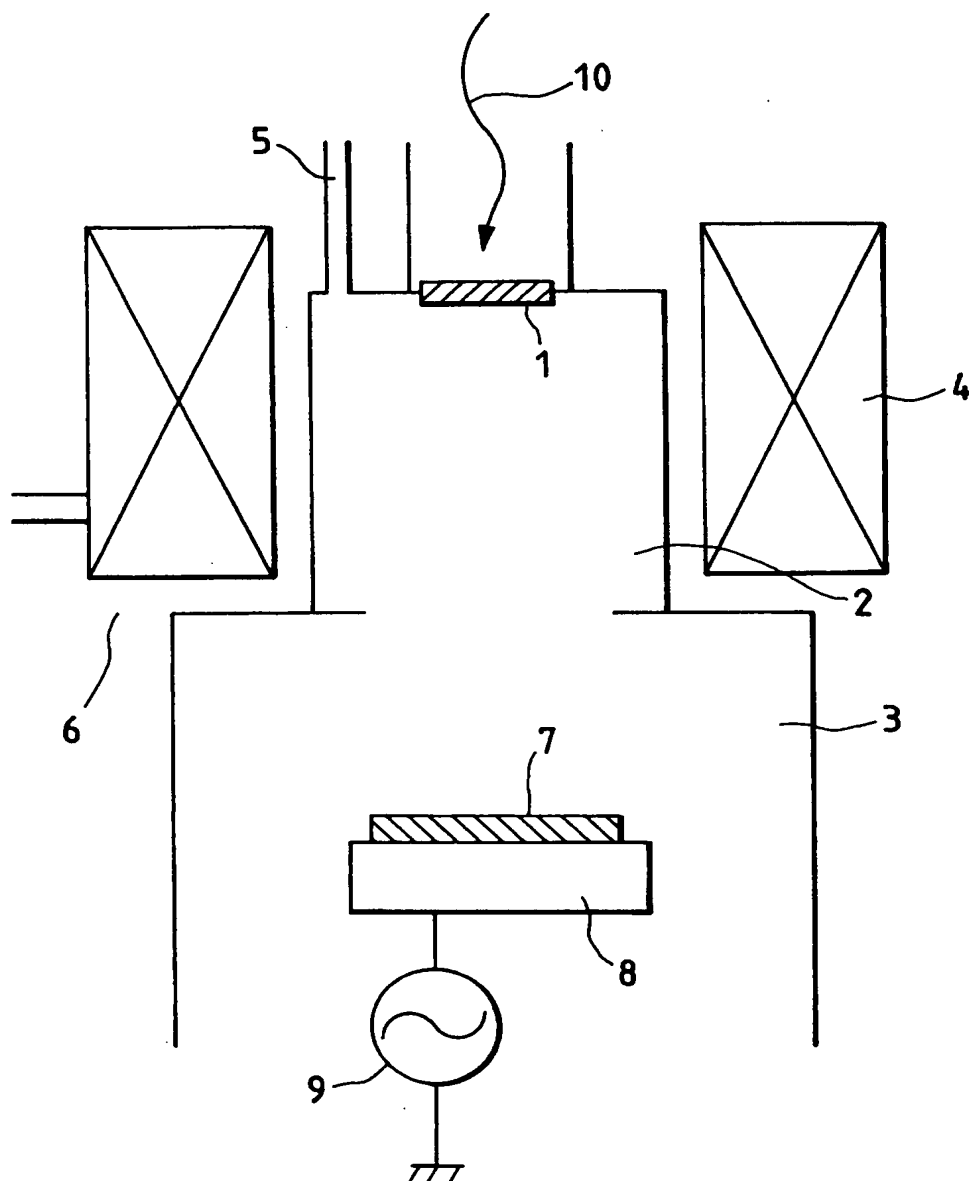


FIG. 11

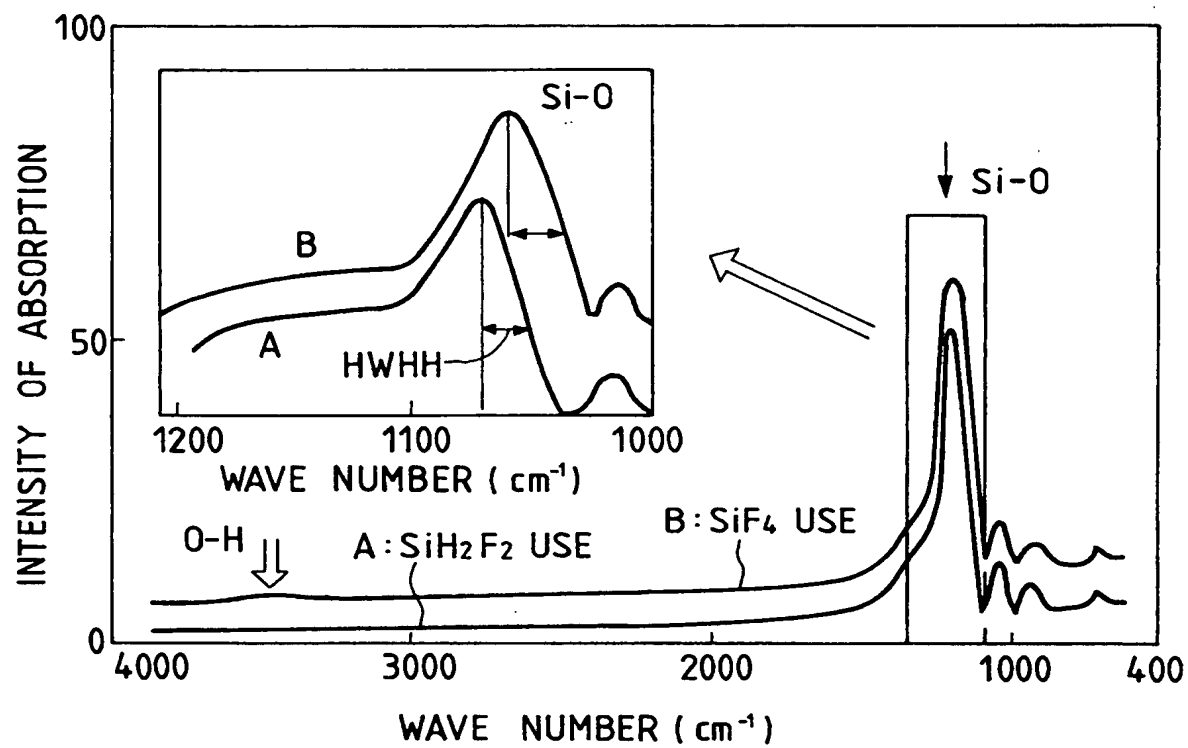


FIG. 12

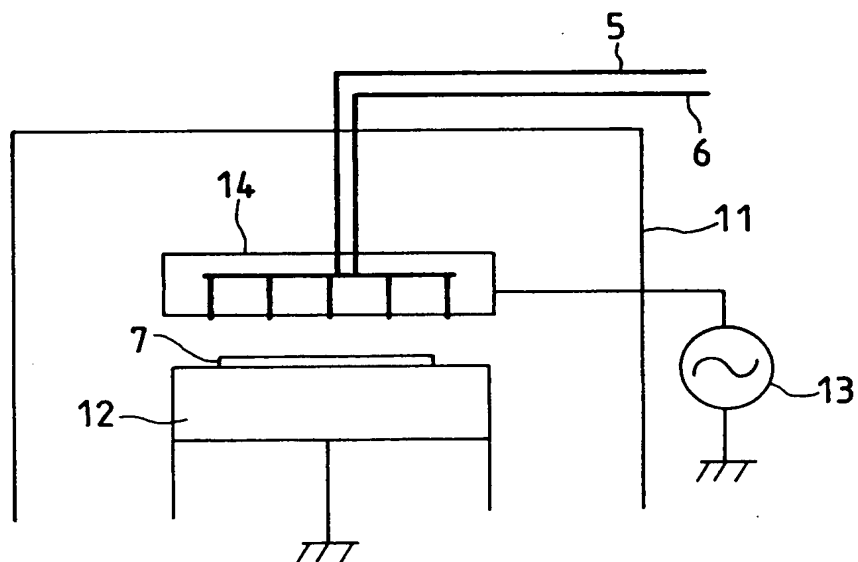


FIG. 13

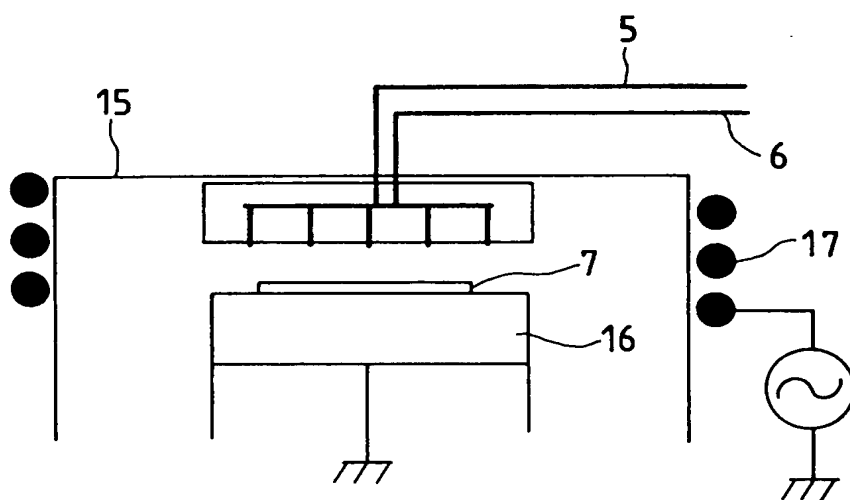


FIG. 14

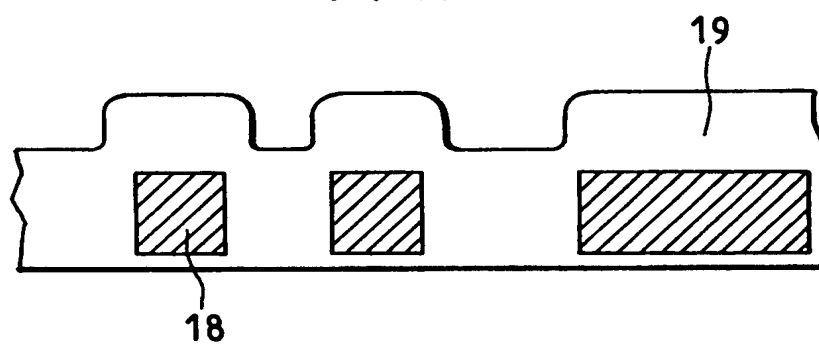


FIG. 15

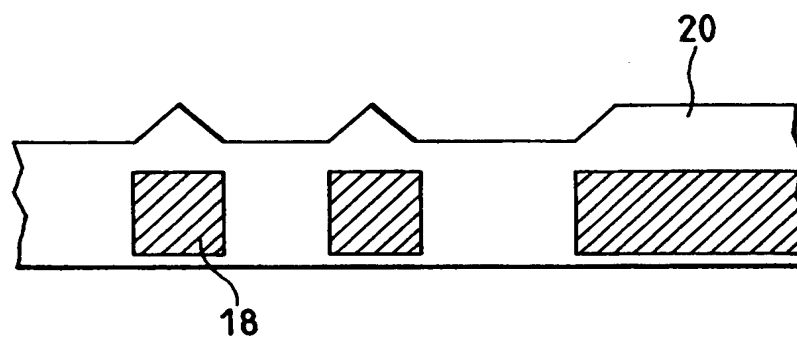


FIG. 16

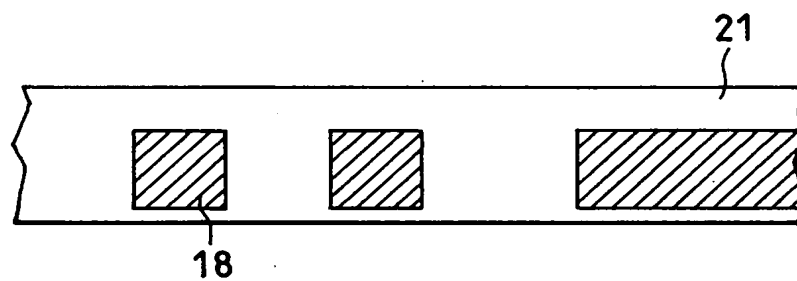


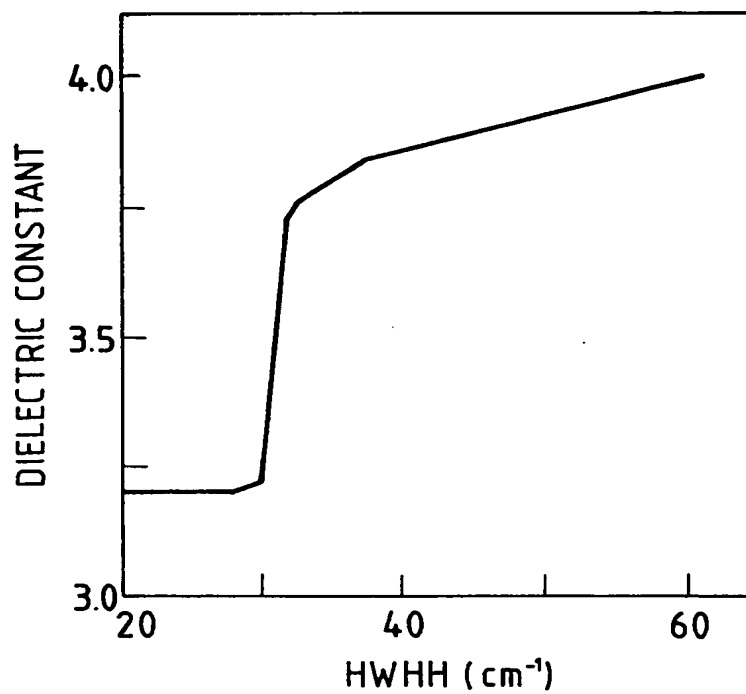
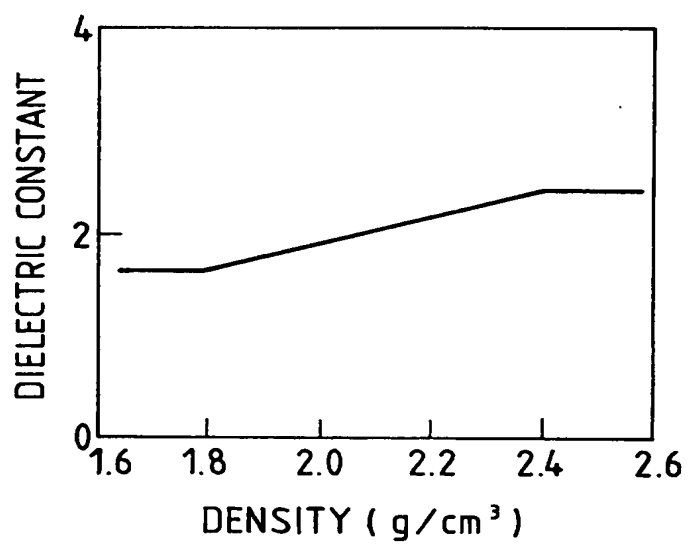
FIG. 17*FIG. 18*

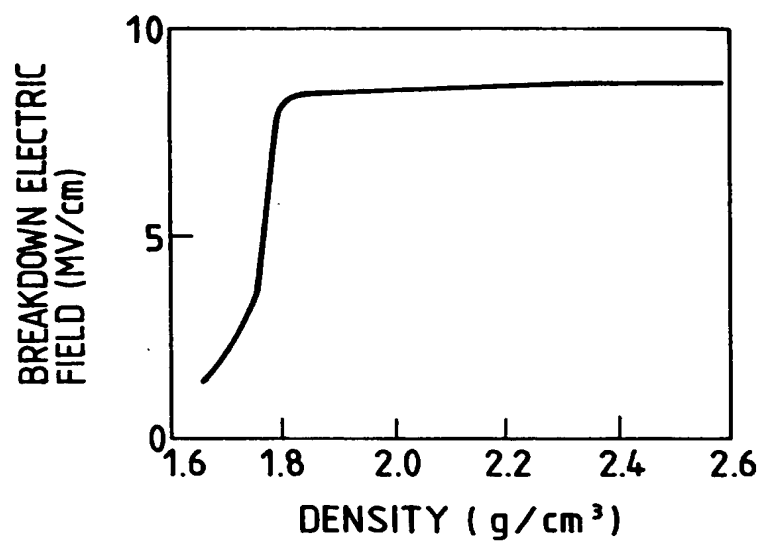
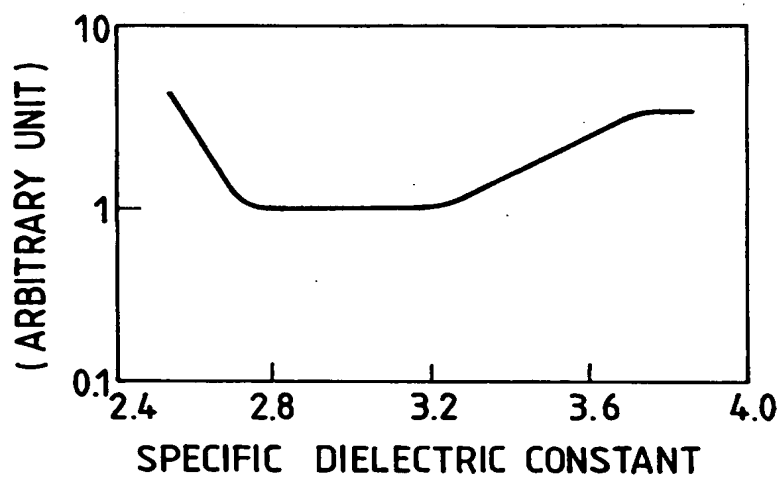
FIG. 19*FIG. 20*

FIG. 21

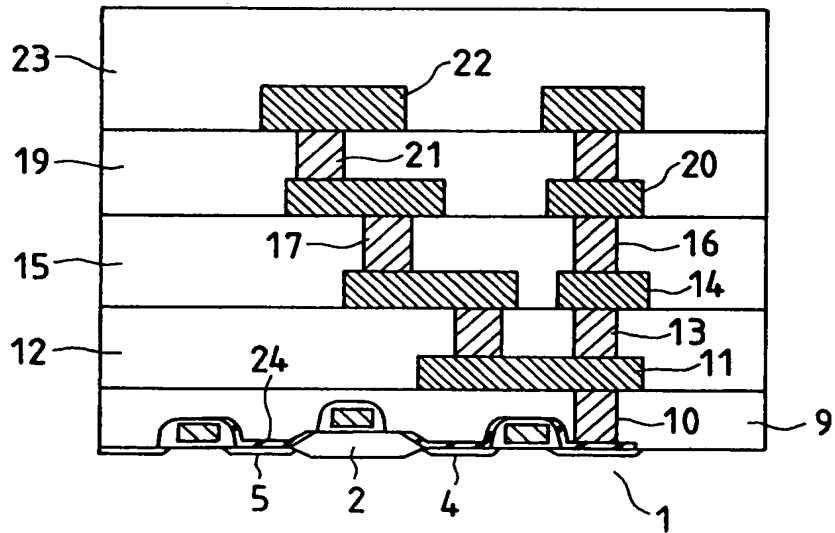


FIG. 22

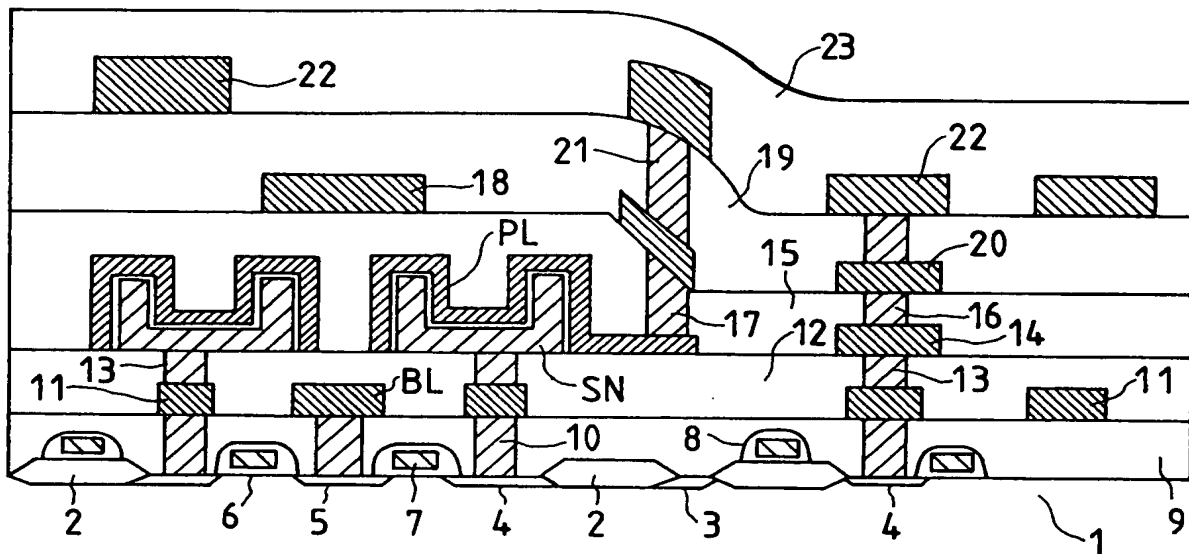


FIG. 23

